THE EFFECT OF OXIDES ON STABILIZATION OF ZIRCONIUM DIOXIDE

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The processes of coprecipitation of calcium, strontium, and cadmium salts are studied. It is shown that alkaline coprecipitation produces zirconates, which in heat treatment form stable solid solutions.

Zirconium dioxide is an indispensable material in the production of condenser ceramics. It is characterized by polymorphic transformations in heating [1], which can be represented in the following form:

$$ZrO_{2(m)} \underset{975-820°C}{\overset{1100-1190°C}{\rightleftarrows}} ZrO_{2(s)} \overset{2285°C}{\rightleftarrows} ZrO_{2(c)}.$$
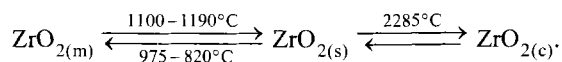
It can be seen that in heating up to 1100°C, the stable monoclinal modification is transformed into a tetragonal one. The monoclinal modification is formed at a temperature of 600 – 750°C from metastable phases. Reversible transformation takes place at a lower temperature and is accompanied by a decrease in volume, which leads to cracking of articles. Therefore, the monoclinal modification needs to be stabilized through its transition to solid solutions of cubic or tetragonal modifications. The stabilizing additive is usually calcium oxide introduced in powder form.

The purpose of the present work was to obtain calcium, strontium, and cadmium zirconates using the precipitation method and to study the effect of RO oxide on the stabilization of ZrO_2 in heat treatment of synthesized compounds.

The reactants used in the study were $CaCl_2$, $Sr(NO_3)_2$, $CdSO_4$, and $ZrOCl_2 \cdot 8H_2O$. Zirconates were synthesized from 0.5-M salt solutions, and precipitation was performed using a 1-M solution of NaOH or a solution of NH_3 (1 : 1). The synthesis and analysis of the compounds were carried out in the same way as in previous studies [2]. The ratio R : Zr(R = Ca, Sr, Cd) was set equal to 1 : 1, and the pouring sequence of the precipitator and salt solutions was direct in all cases.

To obtain data on the possible interaction of two-charge metal ions with zirconium ions in the course of joint alkaline precipitation, pH titration of salt solution by alkali was carried out (an EV-74 universal ionometer with glass and silver chloride electrodes). The values of the products of the solubility of calcium, strontium, cadmium and zirconium hydroxides are 6.5×10^{-6}, 3.2×10^{-4}, 2.2×10^{-14}, and 7.9×10^{-55},

respectively [3]. With such significant differences in solubility levels, zirconium hydroxide and two-charge metal hydroxides should be titrated separately for any salt concentration, i.e. there should be two jumps on the titration curve. In fact, only one jump on curves *1* and *2* (Fig. 1) corresponds to the precipitation process, which clearly points to the chemical reaction of Ca(II) and Zr(IV) and Sr(II) and Zr(IV) ions on adding alkali. The products of such a reaction can be compounds of the type of calcium and strontium zirconates.

It is known that the predominant reaction in coprecipitation processes of hydroxides is acid-base interaction, which can be implemented as ionic exchange, coordination and hemosorption trapping, or the formation of chemical compounds and solid solutions [4]. The criterion used to estimate the relative acidity of hydroxides is ionic potential:

$$\varphi = q/r,$$

where q is the ion charge and r is its radius.

The ionic potentials of the considered ions calculated on the basis of reference data on ionic radii [3] arranged in ascending order are 16.67 (Sr^{2+}) < 19.23 (Ca^{2+}) < 20.20 (Cd^{2+}) ≪ 48.78 (Zr^{4+}). Consequently, the acid properties of hydroxides ascend in the same order. This means that $Sr(OH)_2$, $Ca(OH)_2$, and $Cd(OH)_2$ reacting with zirconium hydroxide can produce salts, since the difference between the values of φ is very substantial: 32.11 for the Sr – Zr system, 29.55 for the Ca – Zr system, and 28.58 for the Cd – Zr system. Indeed, as NaOH is added to calcium and zirconium salt solutions, hydroxides $Ca(OH)_2$ and $Zr(OH)_4$ are formed. The former is an alkali, and the latter is amphoteric. This means that they should enter into an acid-base reaction, which in a simplified form can be represented as the following reaction:
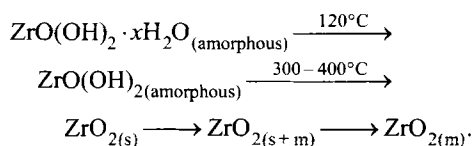
$$Ca(OH)_2 + H_4ZrO_4 = CaZrO_3 + 3H_2O.$$
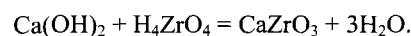
There are two jumps on the titration curve of the mixture of cadmium and zirconium salts (Fig. 1, curve *1*), which does not provide for a unique interpretation of their interaction. However, the low value of the first jump, the distorted second jump, and the very large flattened segment between

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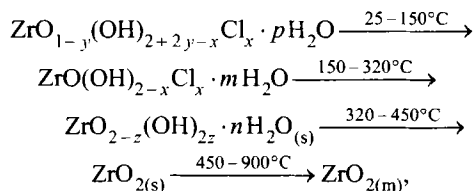[1] Belarus State Technological University, Minsk, Belarus.

them suggest a possible interaction between Cd(II) and Zr(IV) when precipitated by alkali.

The obtained precipitates after washing, filtration, and drying were studied by differential thermal analysis (DTA) on a Paulik – Paulik – Erday derivatograph within the temperature range 20 – 1000°C with a heating rate of 25°C/min (Table 1).

According to the data in [5], hydrated ZrO_2 gel is an amorphous dihydroxide $ZrO(OH)_2 \cdot xH_2O$ which undergoes the following transformations in heat treatment:

$$ZrO(OH)_2 \cdot xH_2O_{(amorphous)} \xrightarrow{120°C}$$

$$ZrO(OH)_{2(amorphous)} \xrightarrow{300-400°C}$$

$$ZrO_{2(s)} \longrightarrow ZrO_{2(s+m)} \longrightarrow ZrO_{2(m)}.$$

In [6], the scheme of chemical transformations of initial xerogel in calcination in represented in the following way:

$$ZrO_{1-y}(OH)_{2+2y-x}Cl_x \cdot pH_2O \xrightarrow{25-150°C}$$

$$ZrO(OH)_{2-x}Cl_x \cdot mH_2O \xrightarrow{150-320°C}$$

$$ZrO_{2-z}(OH)_{2z} \cdot nH_2O_{(s)} \xrightarrow{320-450°C}$$

$$ZrO_{2(s)} \xrightarrow{450-900°C} ZrO_{2(m)},$$

where $0 < y < 1$, $x = 0.2 - 0.7$, $p > m > n$, and $0 < z < 1$.

Based on these data and the DTA curves obtained by us, the energy effects can be attributed to zirconium hydroxide (Table 1).

It is known [7] that in calcination of $Ca(OH)_2$ at 580°C, 1 mole of H_2O is removed. This effect is absent on the DTA curve of the precipitate obtained by the coprecipitation method of calcium and zirconium hydroxides, the same as the effects of crystallization and polymorphic transformation of ZeO_2 at temperatures of 430 and 880°C. This is evidence of the formation of a new chemical compound, different from the individual hydroxides, and this agrees well with the pH titration results.

$Sr(OH)_2$ decomposes at a temperature of 535°C [7]. However, the effect corresponding to this process is absent on the DTA curves of coprecipitated strontium and zirconium hydroxides in using both precipitators, i.e., NaOH and NH_4OH. The exothermic effects typical of zirconium hydroxides are absent as well. The amount of water (5.23 – 5.40 moles) turned out to be significantly greater than the additive value (2.18 from $ZrO_2 \cdot nH_2O$ and 1.00 from $Sr(OH)_2$). Consequently, a solid hydroxide substitutional solution was formed in the specified system [8]. The same is true of the system of coprecipitated cadmium and zirconium hydroxides.

It is established experimentally (Fig. 2) that the amount of removed water for the considered hydroxide systems (ac-

TABLE 1

Compound	Heating rate, °C/min	Precipitator	Temperature of DTA curve effect,* °C	Temperature interval of effect, °C in DTA curve	Temperature interval of effect, °C in DTG curve	Weight loss % initial quantity	Weight loss H₂O quantity, mole	Energy effects
$ZrO_2 \cdot nH_2O$	25	NaOH	150(–)	40 – 340				Dehydration [5, 6]
			430(+)	380 – 480	40 – 440	22.94	2.04	Crystallization [5, 6]
			880(+)	780 – 930	–	–	–	Polymorphic transformation t → m [5, 6]
			–	40 – 1000	–	24.12	2.18	–
$CaO \cdot ZrO_2 \cdot nH_2O$	5	NH_4OH	140(–)	20 – 360	20 – 360	19.64	2.43	Dehydration
			430(–)	360 – 430	–	1.19	0.12	Crystallization
			500(+)	430 – 560	–	1.19	0.12	The same
			625(–)	560 – 700				
			–	20 – 1000	–	23.21	3.01	–
$SrO \cdot ZrO_2 \cdot nH_2O$	25	NaOH	130(–)	20 – 370	20 – 480	23.64	3.90	Dehydration
			565(+)	480 – 640	–	5.68	0.76	Crystallization
					780 – 1000			
			–	20 – 1000	–	29.32	5.23	–
$SrO \cdot ZrO_2 \cdot nH_2O$	25	NH_4OH	180(–)	20 – 420	20 – 460	23.75	3.93	Dehydration
			600(+)	510 – 620	–	–	–	Crystallization
			680(–)	620 – 720	–	–	–	–
			920(+)	850 – 960	820 – 940	1.88	0.24	–
			–	20 – 1000	–	30.00	5.40	–
$CdO \cdot ZrO_2 \cdot nH_2O$	5	NaOH	120(–)	20 – 340	20 – 260	18.29	3.13	Dehydration
			380(–)	340 – 460	260 – 420	8.57	1.31	The same
			550(+)	500 – 600	520 – 610	3.43	0.50	Crystallization
			–	20 – 1000	–	30.29	6.07	–

* The minus sign (–) indicates an endothermic effect; the plus sighn (+) indicates an exothermic effect.

cording to the DTA data) is proportional to the molar weight of the zirconate formed in heat treatment of the precipitate. The knowledge of this dependence has a practical (technological) meaning, since the volume of hydroxide precipitate determines the size of the working reservoirs, the precipitate washing rate, and the water consumed in this operation.

The precipitates calcined at temperatures of 1000, 1100, and 1200°C were investigated by x-ray phase analysis (DRON-2).

The x-ray pattern of heat-treated zirconium hydroxide exhibits reflections related to various modifications of ZrO_2, primarily the monoclinal modification (3.24, 2.92, and 2.60 Å). Reflections of a pseudocubic modification similar to the monoclinal one were identified as well (2.92, 1.85, and 1.56 Å).

The x-ray diffraction diagram of the precipitate consisting of coprecipitated strontium and zirconium hydroxides (Fig. 3) exhibits reflections of $SrZrO_3$ (2.97, 1.82, and 1.43 Å) and SrO (2.56, 2.10, 1.51 Å). The latter is a stabilizer and virtually prevents the transformation of the unstable tetragonal form of ZrO_2 to the monoclinal modification, since the ZrO_2 crystal lattice acquires strong and stables bonds which are not destroyed in heat treatment. Stabilization is accomplished due to the rearrangement of the unstable tetragonal lattice into a cubic one. A substitutional solid solution is formed in this way.

The ionic radius of a stabilizer should be close to the ionic radius of Zr^{4+}. In our case, $r_{Sr^{2+}} = 1.27$ Å and $r_{Zr^{4+}} = 0.87$ Å. Presumably, this results in the formation of a pseudocubic distorted lattice. The degree of stabilization depends on the heat-treatment temperature and the initial materials. When strontium zirconate is produced from precipitates at 1200°C and 1 h holding, SrO and ZrO peaks virtually disappear.

The formation of substitutional solid solution $SrZrO_3$ was observed in all cases (Fig. 3). Judging from the height of the reflections, the reaction at 1200°C using the precipitates is more complete. Only insignificant ZrO_2 reflections (1.80. 1.44, and 1.30 Å) remain. In fact, the entire SrO is implanted into the crystal lattice of ZrO_2 and stabilizes it.

With increasing temperature, more complete formation of $SrZrO_3$ is registered. However, the maximum level of the formation of a substitutional solid solution is already attained at 1100°C. The solution has a cubic lattice, which prevents variations in the linear dimensions of articles made of stabilized zirconium dioxide.

A solid-phase reaction of the formation of $CaZrO_3$ takes place in heat treatment of a sample obtained by coprecipitation of cadmium and zirconium hydroxides. Since $r_{Cd^{2+}} < r_{Sr^{2+}}$, the process of CdO implantation is more intense. First, $CdZrO_3$ arises at a temperature of 1000°C, and then with temperature increasing up to 1200°C, CdO reacts with the main bulk of ZrO_2, and the solid solution of CdO in ZrO_2 is formed.

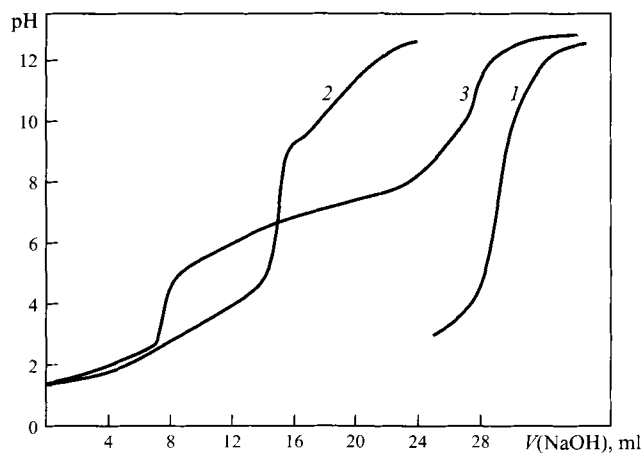Thus, using the coprecipitation method, it is possible to decrease the energy consumed in preparing the mixture, ex-

Fig. 1. pH Titration curve of solutions: 1) Ca(II) – Zr(IV); 2) Sr(II) – Zr(IV); 3) Cd(II) – Zr(IV).
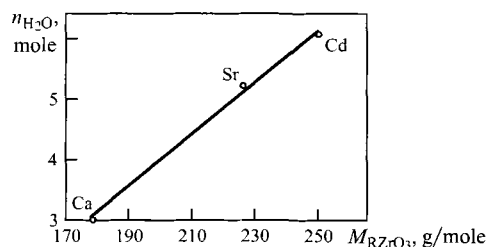

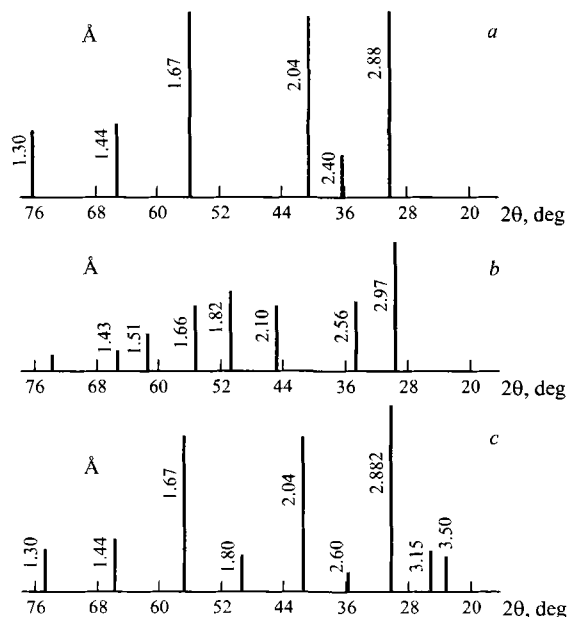Fig. 2. Quantity of water removed in heat treatment versus molar weight of zirconates.

Fig. 3. X-ray diffraction diagrams of strontium zirconate calcined samples: a) 1100°C, sintering of SrO and ZrO powders; b) 1100°C, joint precipitation of hydroxides; c) 1200°C, joint precipitation of hydroxides.

clude milling, and obtain stabilized calcium, strontium, and cadmium zirconates.

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